CHARACTERIZATION AND PROPERTIES OF THERMOPLASTIC TAPIOCA STARCH BASED HIGH DENSITY POLYETHYLENE / NATURAL RUBBER BLENDS

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by

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LIST OF ABBREVIATIONS

APS	γ-aminopropyltriethoxysilane
ASTM	American society of testing and materials
ATS	3-acryloxypropyltrimethoxysilane
CA	Citric acid
COPE	Copolyesters
DCP	Dicumyl peroxides
DCS	Dichlorosilane
DMTA	Dynamic mechanical thermal analysis
DP	Degree of polymerization
DSC	Differential scanning calorimetry
EPDM	Ethylene-propylene-diene terpolymer
EPMA	Ethylene-propylene copolymer
EVOH	Poly(ethylene-co-vinyl alcohol)
FTIR	Fourier transform infrared spectoscopy
GPS	Glycidoxypropyltrimethoxy
HDPE	High density polyethylene
HDS	Hexadecyltrimethoxysilanes
HPLC	High performance liquid chromatography
HVA-2	N, N'-m-phenylene bismaleimide
LDPE	Low density polyethylene
LLDPE	Low linear polyethylene
MBTS	2,2'-Dibenzothiazole Disulfide
MFI	Melt flow index
MPS	γ-methacryloxypropyltrimethoxysilanes
MRPS	γ-mercaptopropyltrimethoxysilanes

NaOH	Sodum hydroxide
OBC	Olefinic block copolymers
OSA	Octenyl succinic anhydrides
PBS	Polybutylene succinate
PCL	Polycaprolactone
PE	Polyethylene
PEBA	Polyether block amides
PEGMA	Poly(ethylene-co-glycidyl methacrylate)
PE-g-MA	Polyethylene-grafted-maleic anhydride
PHA	Polyhydroxyalkanoate
Phr	Part per hundred rubber
PLA	Polylactic acid
POE	Polyolefin elastomer
PP	Polypropylene
PPDO	Poly(1,4-dioxanone)
PP-g-MA	Polypropylene-grafted-maleic anhydride
PS	Polystyrene
PVA	Poly(vinyl alcohol)
PVC	Poly(vinyl chloride)
RF	Resorcinol formaldehyde
RI	Refractive index
RTR	Reclaimed tyre rubber
SBC	Styrenic block copolymer
SBR	Styrene butadiene rubber
SEBS	Styrene-ethylene-butadiene-styrene
SEM	Scanning electron microscope
SMR	Standard Malaysian rubber

TBBS	N-tertbutyl-2-benzothiazole sulfenamide
TGA	Thermogravimetric analysis
TMTD	Tetramethyl thiuram disulfide
TPE	Thermoplastic elastomer
TPNR	Thermoplastic natural rubber
TPO	Thermoplastic polyolefin
TPS	Thermoplastic starch
TPSCA	Thermoplastic starch modified with citric acid
TPU	Thermoplastic urethanes
TPV	Thermoplastic vulcanizates
VSPE	Vinyltrimethoxysilane grafted polyethylene
VSPP	Vinyltrimethoxysilane grafted polypropylene
VTS	Vinyltrimethoxysilane
ZnO	Zinc oxide

LIST OF SYMBOLS

µm	Micrometer
dH	Total crystallization enthalpy
dt	Crystallization enthalpy from initial time to time t
E'	Storage modulus
E''	Loss modulus
E_b	Elongation at break
K	Crystallization rate of Avrami equation
kg	Kilogram
kJ	Kilojoule
mW	Heat flow
n	Avrami exponent
R	Universal gas
r	Cooling rate
Z	Crystallization rate
$T_{5\%}$	5% weight loss temperature
$T_{90\%}$	90% weight loss temperature
Tan δ	Mechanical loss factor
T_c	Crystallization temperature
T_g	Glass transition temperature
T_m	Melting temperature
W	Watt
Wf	Weight fraction
Wt	Weight
X (t)	Fraction volume of crystallization
X_c	Crystallinity degree

ΔE_o	Crystallization energy
ΔH_m	Heat of fusion
ρ	Density

PENCIRIAN DAN SIFAT-SIFAT ADUNAN POLIETILENA BERKETUMPATAN TINGGI / GETAH ASLI BERASASKAN THERMOPLASTIK KANJI UBI KAYU.

ABSTRAK

Kesan termoplastik kanji ubi kayu (TPS) ke atas sifat-sifat adunan polietilena berketumpatan tinggi (HDPE) / getah asli (NR) (70/30) telah dikaji. Kanji ubi kayu telah dipilih untuk digabungkan ke dalam adunan HDPE / NR disebabkan mudah diperolehi dan bersifat terbiodegradasi. Walau bagaimanapun terdapat masalah seperti tahap keserasian yang rendah dengan matriks polimer yang bersifat hidrofobik, kecenderungan untuk tidak tersebar semasa pemprosesan dan keafinan terhadap lembapan merupakan faktor-faktor yang mengurangkan potensi adunan berasaskan TPS. Variasi pembebanan TPS dari 0 wt% hingga 30 wt% dan dimasukkan ke dalam adunan HDPE / NR menggunakan pencampur dalaman HAAKE rheomix 600. Pengadunan leburan telah dijalankan pada suhu 150 °C dengan kelajuan rotor 50 rpm selama 12 minit. Fungsi pembebanan TPS dan kesan modifikasi adunan diukur ke atas sifat mekanikal adunan. Kekuatan tensil menunjukkan penurunan yang ketara disebabkan ketidakupayaan TPS untuk menyokong pemindahan tegasan antara fasa. Beberapa siri modifikasi telah dijalankan dalam usaha meningkatkan sifat-sifat mekanik adunan. TPS telah dirawat dengan asid sitrik untuk meningkatkan tahap kebelandiran dan keplastikan TPS dalam adunan HDPE / NR. TPS boleh dinyahpolimer sebahagiannya untuk menghasilkan produk berkelikatan rendah apabila diproses dengan asid sitrik. TPS dengan berat molekul (M_w) yang rendah didapati lebih mudah tersebar di dalam adunan elastomer termoplastik (TPE) dan membaiki tahap pembasahan antara fasa

TPS-HDPE/NR seperti yang ditunjukkan oleh mikroskop pengimbas elektron (SEM). Kesan polietilena-tergraf-malik anhidrida (PE-g-MA) sebagai penyerasi telah menunjukkan peningkatan kekuatan tensil yang berkesan. Tahap pelekatan dan penyebaran TPS dalam adunan bertambah baik bagi adunan yang diserasi dengan PE-g-MA. Kajian SEM menunjukkan peningkatan lekatan antara muka adunan yang jelas untuk adunan TPS-HDPE/NR yang diserasi dengan PE-g-MA. Dalam kes sistem pemvulkanan dinamik, dua siri telah disediakan; (a) adunan sulfur tervulkan dan (b) adunan N, N'm-phenylenebismaleimide (HVA-2) tervulkan HDPE / NR / TPS. Adunan HDPE/NR/TPS yang mempunyai kedua-dua sambung silang menunjukkan peningkatan kekuatan tensil, modulus Young dan pemanjangan pada takat putus yang ketara. Selain itu, mikrograf SEM menunjukkan TPS halus yang tersebar dan terbenam dengan baik di dalam matriks HDPE/NR tervulkan. Perbandingan juga dibuat berdasarkan keputusan kandungan gel, analisis termogravimetri (TGA) dan kalorimetri imbasan pembezaan (DSC). Secara amnya, peningkatan yang diperolehi dalam sifat-sifat tensil, kehomogenan adunan dan kestabilan terma dapat dikaitkan kepada pembentukan taut silang dalam fasa getah asli.

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ABSTRACT

Effects of thermoplastic tapioca starch (TPS) on the properties of HDPE/NR (70/30) blends were investigated. Tapioca starch was chosen to incorporate into HDPE/NR blends due to its abundance and biodegradability properties. However certain drawbacks, such as poor compatibility with the hydrophobic polymer matrix, tendency not to disperse during processing and affinity for moisture are factors which lower the potential of TPS based blends. TPS loadings were varied from 0 wt% to 30 wt% and incorporated into HDPE/NR blends using HAAKE rheomix 600 internal mixer. The melt blending was carried out at temperature of 150 °C with the rotor speed of 50 rpm for 12 minutes. Mechanical properties of blends were evaluated as a function of TPS loadings and the influence of blend's modification. The tensile strength showed a sharp drop on addition of TPS particle into the blends system due to the inability of TPS to support the stress transfer between phases. Few series of blend's modification have been done in order to improve the mechanical properties of the blends. TPS was treated with citric acid in order to improve the plasticization and fluidity of TPS in HDPE/NR blends. TPS can be partly depolymerised to produce low viscosity product when processed with citric acid. It is also found that TPS with low molecular weight (M_w) is easy to disperse in the thermoplastic elastomer (TPE) blend and improve wettability at the inter phase of TPS-HDPE/NR as shown by scanning electron microscope (SEM). The effect of polyethylene-grafted-maleic anhydride (PE-g-MA) as a compatibilizer was also

shown to be effective in improving the tensile strength. The degree of TPS adhesion and dispersion in blends were improved in the cases of PE-g-MA compatibilized blends. The improvement in compatibilized TPS-HDPE/NR interface adhesion was clearly indicated in SEM study. In the cases of dynamic vulcanization system, two series were prepared; (a) sulphur vulcanized blends and (b) N, N'-m-phenylenebismaleimide (HVA-2) vulcanized HDPE/NR/TPS blends. Tensile strength, Young's modulus and elongation at break exhibit significant improvement when HDPE/NR/TPS blends were subjected to the both crosslinkers. Moreover, SEM micrographs showed fine TPS was dispersed and well embedded in vulcanized HDPE/NR matrix. Comparison was also made based on the results of gel content, thermogravimetric analysis(TGA) and differential scanning calorymetry (DSC). Generally, the improvement observed in tensile properties, blends homogeneity and thermal stability can be correlated to the crosslink formation within the NR phase.

CHAPTER 1

INTRODUCTION

1.1 Brief History and the Latest Development of Thermoplastic Elastomer

Thermoplastic elastomers (TPEs), despite their relatively short history as compared to conventionally used materials such as wood and metal, have become dominant choice for many applications. Nowadays, they are used in a wide range of applications which require challenging material properties. In order to cope with the increasing need for development of newer materials, blending multiple polymers is often used to tailor the material properties. TPEs are the materials that combine many favourable characteristics of thermoplastics and elastomers are growing fastest in polymer industry and have tremendous growth in the future. TPEs exhibit hard and soft domains from thermoplastic and elastomeric phase are derived from block coplymers, rubber – plastics blend and ionomers.

TPEs era began with the advent of block copolymers and is first introduced in the 1950s (Schollenberger et al., 1958) which is based on polyurethanes. In the early stage of their development, TPEs are introduced as an alternative to vulcanized rubber industry. Later in 1965, the announcement of the commercial product derived from styrenic block copolymers (Bailey et al., 1966) and since then TPE has gained significant interest in rubber industry. Besides utilizing copolymers and ionomers, another variation in preparing TPEs is via rubber – plastic blend or dynamic vulcanization. Blended TPEs contain elastomeric as a disperse phase in thermoplastic phase, which is typically polyolefin resin. They can be melt-processed numerous

times and have broad range of properties by merely changing the blend ratio. TPEs which belongs to this group is easy to process in typical thermoplastic processing equipment such as extruders and injection moulders. The ability to reground and reuse the TPE scraps and reject parts, shorter processing time with less or no compounding additives are required (Ibrahim & Dahlan, 1998) to transform it into an attractive option for plastic manufacturers.

The unique feature of TPEs which exhibit the characteristics like conventional vulcanized rubber, but without going through the vulcanization process are attractive that renders the TPEs to become commercially successful. Nowadays, there are severals improvement in processing and production of TPEs that allow them to be used in many applications including hard packaging, the automotive and medical industries. Automobile industry will be the biggest market for TPEs with the demand forecast to rise to 1.2 million metric ton in 2013. By the year 2015, Asia Pacific region is expected be to the largest growing market for TPEs accounting for half of world's demand (www.freedoniagroup.com). TPE market is outburst with ongoing demand in producing less vehicle weight, particularly regarding in the realm of economical standard on account of the rise in oil price.

1.1.1 Thermoplastic Elastomer Based on Polyolefin and Natural Rubber

Polyolefin such as polyethylene (PE) and polypropylene (PP) have interesting mechanical properties such as good ductility and high thermal stability; as well as poses excellent moisture and chemical resistance. Another advantage over many other polymers is low density, relatively low cost and derived from the readily available simple monomer which makes it currently the most versatile commercial

polymers. However its usage was limited by low impact resistance especially at low service temperature. Blending with low modulus natural rubber (NR) as scattered phase is considered to be an impact modifier in tough polyolefin resin. A blend with combination of these systems commonly known as thermoplastic natural rubber (TPNR) gives rise to a new material which exhibit good mechanical properties and improve the impact resistance. Another desirable properties found in TPNR are excellent thermal stability, a good moisture and chemical resistance and poses good tensile properties.

Thermoplastic natural rubber, based primarily on polyolefin (PP and PE) and NR are one of the important families of thermoplastic elastomers (TPEs). Styrenic block copolymers (SBCs), which is a leading TPEs family is limited by the high degree of market saturation in many applications. Whereas, TPEs based on olefenic natural rubber is growing fastest and used extensively in automotive market. The demand for olefenics natural rubber is expected to continuously increase and penetrating the automotive markets in both interior and exterior applications. They have largely replaced the materials use in bumper parts, exterior and interior trim and also used as a replacement for expensive copolyesters in airbag covers (Rouif, 2004; Lorentzen, 2005; Drobny, 2007; Mike, 2008; Markarian, 2009). However, soft olefenic natural rubber will enjoy the growth in markets for producing moulded goods, soft toys, soft grip tools, medical and some other newer applications (Ausias et al, 2007; Markarian, 2008; Golaz et al., 2011).

1.2 Environmental Impact: Industrial Waste Polymer Disposal.

Plastics based products are light, versatile and long lasting indestructible material which makes it ideal for daily use. Plastics have become a substitute for many items which used to be made from other materials, such as a replacement for the aluminium cans and glassware. The abundance of plastics materials available at the cheap price makes it an attractive option for household use. Besides easily available, plastic has caused many environmental downsides, starting from the production of plastics until the problem of waste disposal. Commercial plastic today is based on the petroleum and natural gas sources.

The actual problems appear when it comes to the waste disposal. The vast majority of plastic products, especially packaging materials winds up in landfills. Besides the fact that available landfill space is becoming increasingly scarce, plastic poses special problems for landfills. Most plastic materials are non-biodegradable which means that it does not easily break down to be naturally decompose. Besides the most plastic materials waste end up at the landfill, some proportion of the plastics waste also winds up in the ocean. When the plastics waste are not properly handled and toss everywhere, the rain water will move it until it lands in a stream and eventually end up in the ocean. Nowadays it can be seen that every ocean in the world has plastic trash in it. This causes a serious problem to the ecosystems and threatens the food chains which later eventually end up in the human diets.

Besides the conventional way for disposing of plastic materials in landfill, there is some suggestion that promoting disposal of plastics waste via incineration. Incineration is the process to burn plastics into hydrocarbon soup which later can be

reused in oil or as a material for energy source. However incineration is not the best choice due to involving an expensive process and it is also creating severe air pollution problems.

As a response for the environmental issues, blending synthetic polymer with a cheap natural biopolymer from the natural bio-based plant provides new attention to manufacture biodegradable or semi biodegradable products. Most commonly used are cellulose and starch. Incorporation of cellulose and starch into synthetic polymer, which enhances the environmental fragmentation and degradation have been investigated by many researchers (Chandra & Rustgi, 1997; Bikiaris et al., 1998; Huang et al., 2005; Shi et al., 2007; Ning et al., 2007; Raquez et al., 2008). This new generation of bio-based plastic can compete in the market which is currently being dominant by the products based on petroleum feedstock.

1.2.1 Polysaccharide as a Partial Replacement in Petroleum Based Products

In the context of the increased problems associated with our environment, the utilization of natural resources as a viable alternative for conventional plastics has attracted more attention from the academician and also industry. In this scenario, it is not necessary for producing 100% of biodegradable materials as substitution of petroleum based products immediately, but a partial replacement also could help to save our environment. Economical problem associated with expensive process for producing biodegradable polylactic acid (PLA), polyhydroxyalkanoates (PHAs) polycaprolactone (PCL), polybutylene succinate (PBS) and low mechanical properties of inexpensive thermoplastic starch (TPS) makes the production of fully biodegradable materials difficult. A viable solution is to combine different features

and benefits from both petroleum and bio-resources based materials to produce useful products having the requisite combination of cost-performance properties for real world applications.

Blending polysaccharide with synthetic polymer could also be the promising alternative to the commonly used conventional filler reinforce composite polymer. The combination of polysaccharide, i.e cellulose and starch with synthetic polymer to produce newer materials that are competitive with synthetic polymer reinforced with conventional filler such as glass fibre, glass bead, carbon black, silica, etc, is gaining attention over the last decade. The advantages of natural filler from the renewable plant source over the conventional fillers are as follows: lightweight, low cost, abundantly available, ease for separation, acceptable mechanical strength and biodegradable. Environmental friendly materials have the potential to be the new materials in the future and could be the partial solution to the many environmental problems.

Since, the natural resources based filler is biodegradable and conventional thermoplastic like polyolefin is non-biodegradable, the combination of these two materials is classified as partially biodegradable system. Upon exposure to the microbial activities, the starch based materials is weakened as a result of degradation and thus leading to a partial breakdown process refereed to as biofragmentation (Vallini et al., 1994). Production of partially or fully biodegradable materials has offered the possible solution to the polymer waste disposal associated with the petroleum based plastics. However, the true challenge in producing new materials based on biocomposites is to design the materials which could level the mechanical

properties of the existing conventional composites, and yet are susceptible to the microbial and environmental degradation upon disposal without any adverse effect on the environment.

1.3 Research Background of the Present Work

Recent concern over environmental impact caused by plastic waste disposal has motivated the need for new biomaterials and more sustainable and green technology approach. In the polymer community, the awareness about environmental degradation, the use of natural derived plastic versus petroleum derived plastic, the low cost of abundantly natural fibre against the acceptable mechanical properties have created continuous interest on the new sustainable materials which is one or more components is biodegradable or bio based polymer.

A common ways to reduce the complications associated with biodegradable polymer is through the polymer blends. Polymer blends provide a simple and cost productive process to create new materials with combination of biodegradable and acceptable properties. This current work falls under the green polymer blends consisting tapioca starch as one of the blends component. This material is used as a native starch or in modified thermoplastic form and blends with TPNR which is composed of HDPE and NR. Many works have established its usefulness based on granular starch as a filler to enhance biodegradation of conventional plastics such as low density polyethylene and high density polyethylene, polypropylene and polystyrene (Rodriguez-Gonzalez et al., 2003; Huang et al., 2005; Rui Shi et al., 2007; Ning et al., 2007; Raquez et al., 2008; Chiu et al., 2009; Prachayawarakorn et al, 2010). However, different with cellulose fibre which is exhibit rigid and fibrous

materials, starch are in granular type with the backbone created of α-D-glucose linkages and appear as inert filler in polymer blends. The creation of new materials based from starch blends often exhibit a range of complications beginning with reduction in the strength of properties, hydrophobicity and incompatibility with most of conventional polymers (Smith, 2005).

In the starch based polymer blend, the overall properties and characteristics depend upon the dispersion of the dispersed size. Since the mixing of starch with secondary polymer is limited by the agglomeration of starch particle at higher concentration, most of the previous works have used starch as a dispersed phase in which the concentration is in the range of 5% - 30% (Yang et al., 1996; Abdul Khalil et al., 2001; Jayasekara et al., 2004; Huang et al., 2005; Sailaja, 2005; Jiang et al., 2006; Liu et al., 2008; Abdul Majid et al., 2010). Several methods have been applied to compatibilized the blends and thus improve the dispersion of starch in polymer matrix. To overcome this incompatibility problem and to generate melt blending with small dispersed phase as well as to reduce interfacial tension the use of compatibilizer becomes one of the attractive options. Among numerous compatibilizers that are being studied, polyethylene grafted maleic anhydride (PE-g-MA) and polypropylene grafted malice anhydride (PP-g-MA) are known as effective compatibilizers on the blends with polyolefin (Bikiaris et al., 1998; Chandra & Rustgi, 1997; Huang et al., 2005). A successful compatibilization has to meet at least one of these criteria: reducing interfacial tension between the phases, stabilizing the morphology structure during the melt process, increasing the surface adhesion and thus can facilitate the stress transfer between the phases.

On the other hand, to produce blends which can meet the desired properties, this study also focussed on the NR vulcanize using dynamic vulcanization. Dynamic vulcanization process is a promising method in improving the mechanical properties of thermoplastic natural rubber (TPNR) blends. It involves the NR particle being crosslinked in the molten unvulcanized thermoplastic and leading to significant alteration in the mechanical properties of the resulting blends. This work is intended to crosslink intra- and intermolecular bonds in NR polymer chains, and thus increases the stability and strength of the NR phase. Besides sulphur or sulphur derivative, dynamic vulcanization process can also be performed by utilization of bismaleimide such as m-phenylene bismaleimide (HVA-2).

1.4 Problem Statement

Most of the plastic products are made from petroleum based plastics which are not biodegradable or discompose naturally. Therefore disposing of these materials attracts major attention regarding the sustainability issue and demanding continuous developments of producing new biodegradable or semi-biodegradable end products. Starch, being most commercially available products has gained promising attention as a partial replacement for petroleum based plastics and is intensively studied in synthetic polymer – starch blends over the last decade. However, the conversion of agriculture based products into consumer end products is not straightforward due to lack of certain properties which is mandatory in the consumer end products. For instance starch does not posses high mechanical strength and act as inert filler in polymer blends, and thus the properties is reduced with increase in starch content. Other problems are that they do not exhibit good thermal

stability and poor water resistance which creates the compatibility problem with hydrophobic synthetic polymer.

Contrary to their biodegradable behaviour, the mechanical properties of starch based blends are quite poor with increasing starch content. This is attributed to the poor interfacial adhesion due to the incompatibility of hydrophilic starch with hydrophobic synthetic polymer (Bikiaris et al., 1998; Averous et al., 2000; Avella et al., 2000; Huang et al., 2005). Because of inherent hydrophilic nature of starch, the development of starch-plastic blends is having difficulties in achieving good distribution of starch particles in nonpolar matrix and good interfacial adhesion to ensure the effective load transfer between the phases. Different methods have been proposed to improve the incompatibility problem from either modifying starch chemically or physically or the use of compatibilizer.

To date, none of the information on TPS-thermoplastic natural rubber (TPNR) blend has been published elsewhere. Therefore, this work is carried out to study the possibility of producing TPS-TPNR blend, composed of high density polyethylene (HDPE), natural rubber (NR) and thermoplastic tapioca starch. The HDPE/NR-TPS miscibility, mechanical and thermal properties as well as the resistant of the blends towards water are investigated with different compositions.

1.5 Objectives of Study

The objectives of this study are broken down into the following goals:

1) To compare the effectiveness of native starch, modified starch and thermoplastic starch to serve as one of the blend's component in HDPE/NR matrix.
2) To examine the effect of TPS loading on the mechanical properties of HDPE/NR blends and study the effect of starch plasticization, blend's morphology and kinetics crystallization of the blends.
3) To elucidate the effect of PE-g-MA as a compatibilizer on the blend's morphology, water absorption characteristics, mechanical and thermal properties of HDPE/NR/TPS blends.
4) To investigate the effect of modified TPS with citric acid on the TPS particles size distribution in HDPE/NR matrix as well as their end results on mechanical properties.
5) To analyze the reinforcement effect of NR vulcanized on the mechanical properties of HDPE/NR/TPS blends via dynamic vulcanization.

1.6 Organization of the Thesis

This thesis has been divided into eight chapters. Each chapter covers the research interest as mentioned under the objectives of study section.

- **Chapter 1** deals with the introduction of the thesis. It contains brief introduction about the history of TPEs, the problems created with the polymeric materials disposal, green technology approach by blending starch with conventional polymer, research background and problem statement.

- **Chapter 2** contains the fundamental concept related to the starch based polymer blend and presents the literature review on the blend modification in order to better understand the relationship between blend's components.
- **Chapter 3** describes the sample preparation and experimental technique to characterize and evaluate the properties of finished blends.
- **Chapter 4** discusses the preliminary study and determines the optimum blend ratio for HDPE/NR. The study was being continued with the application of starch in HDPE/NR blends either in the form of native or modified starch or in thermoplastic likes. TPS are found to favor the properties of the blends and the subsequent studies are focused on the blending TPS with HDPE/NR.
- **Chapter 5** discusses the use of polyethylene grafted maleic anhydride as a compatibilizer in order to improve the incompatibility at the interface of thermoplastic starch and HDPE/NR.
- **Chapter 6** discusses the plasticization of TPS affected by adding small amount of citric acid. Effects of low viscosity of TPS as a dispersed phase are compared to control TPS in term of structural morphology, tensile and thermal properties.
- **Chapter 7** addresses the improvement of blends strength by vulcanizing the NR phase via dynamic vulcanization. Two different systems were used, namely; sulphur curative system and HVA-2 crosslinker and the results were compared to control HDPE/NR/TPS blends.
- **Chapter 8** concludes the findings of this research which includes several important observations, differences and similarities between the systems used in the blends as well as the achievements in improving the blends properties. Our perspective and future directions of this study are also explained.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter discusses the characteristics and properties of the entire component used in the blends. It further elaborates the development of new materials using starch based blends. The current revolution for green plastics technology to produces new materials properties comparable to their conventional plastic counterparts and coupled with the added advantage of biodegradability. A literature survey was done in the various work related to the starch based blends, particularly related to the blend with polyolefin and natural rubber.

2.2 Polymer Blends

Polymer blends have played significant role in the last few decades in providing high performance alternative to pure polymer. The term ‘polymer blends’ may be defined as a physical mixture of two polymers or two copolymers, giving rise to materials with a range of properties, which could not be delivered by any of the constituents. Polymer blending provides a simple and inexpensive process to combine properties of blend’s components and has the advantages of obtaining them in one product. In addition, the properties of blends can be adjusted by simply changing the blends composition.

In polymer blends, the final properties of resulting products are not only dependent on their constituent component but also strongly related to their morphology as well. The two common morphologies that can be found in polymer blends are; a) a dispersed phase, typically observed as spherical particle in matrix, and b) co-continuous phase, where neither of the blend's component is dominant. Several parameters that can influence the morphology of the resulting blends are composition ratio, viscosity ratio, processing method and the type of flow. In addition to these parameters, the role of interfacial property is also critical. Interfacial interaction characteristics are determined by the miscibility between the blend's components. Most of the polymer blends are immiscible and this feature can lead to poor interfacial adhesion and mechanical properties. However, these immiscible blends are preferable over the miscible blends since the properties obtained in immiscible blends are the combination of individual components, while in case of miscible blends only an average of individual properties are obtained (Olabisi et al., 1978).

As mentioned earlier, most of the commercial polymer blends are immiscible especially the blends between synthetic and bio-based polymer. Poor physical interaction between two immiscible phases results in phase separation under stress, and thus leading to poor mechanical properties. These issues are now addressed using the new blend's technology or strategies that have been discovered and applied by either improving blends processing, or modifying blend's components or, by adding compatibilizer in order to ensure the blends compatible and resulting in improving the physical or chemical interactions across the phase boundaries.

2.3 Blend's Components

In polymer blends, it is possible to improve the blend properties and characteristics such as yield stress, modulus, impact strength, and biodegradability by choosing an appropriate combination of blend's components. For typical semi-biodegradable polymer blends, generally it is composed of the combination between polymer matrices, such as from thermoplastic and/or elastomer and another component as biodegradable agent. Based on the prerequisite characteristics, common semi-biodegradable materials can be classified as bio-composites, where biodegradable agent act as a filler, and binary or ternary blends, when biodegradable agent exist in plasticized form. In this section, the detailed descriptions of blend's component especially related to the polyethylene, natural rubber and starch is presented.

2.3.1 Structural and the Production of Polyethylene

Polyethylene falls under the category of polyolefin polymers which are thermoplastic and having ethylene, $CH_2=CH_2$ as a basic monomer. While the common name for the monomer is ethylene, the commercial name is known by the name ethane, such that polyethylene is also referred as polyethene or polythene (www.lairdplastics.com/product/materials/polyethylene). Polyethylene can be made into soft and flexible, as well as tough, hard and sturdy products. It can be found in many applications of all dimensions form simple to complicated design. Moreover, it can also be turned into everyday use objects, hard and flexible packaging, pipes and toys. Different types of polyethylene are produced under different processing condition depending on the physico-chemical properties of the desired products.

Under the right temperature condition, pressure and catalyst, the ethylene monomer open up and link with other monomers to form long chains of polyethylene. In the commercially available polyethylene, the monomer repeat units range from 1000 to 10000 with its molecular weight ranges from 28000 to 280000 (Charles, 2010). Structural parameters such as density / crystallinity, molecular weight and its distribution, short and long side chains are the key that controll the properties of polyethylene. Manufacturing of polyethylene are usually categorized into "high pressure" and "low pressure" condition. High pressure processes are recognized as that producing low density polyethylene (LDPE), while low pressure is used for producing high density polyethylene (HDPE) and low linear polyethylene (LLDPE). The different grades of the polyethylene are depicted in Figure 2.1.

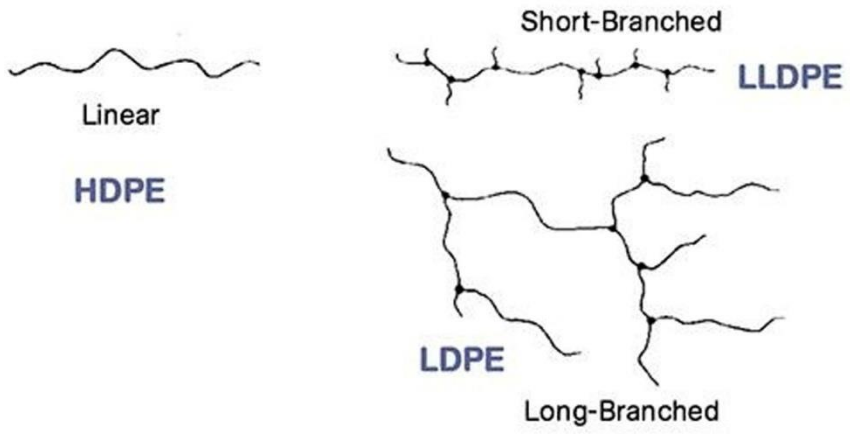


Figure 2.1. A schematic model representative of HDPE, LLDPE and LDPE.

Commercial LDPE is produced at high pressure (15,000 to 50,000 psi) and temperature at around 350 °C. LDPE contains long chains branching in order 1 -3 per 1000 units of carbon atoms as well as short 10 – 30 chains branching per 1000 C. It exhibits low modulus and tensile strength and medium impact and tear resistance

(Zhang and Jia, 2004). Due to the presence of the branches, the polyethylene chains are not closely packed, leaving voids and subsequently producing a material which has a low crystallinity (50% is amorphous) and the sheet allow the flow-through of liquids and gasses. At room temperature, LDPE is insoluble in most of the organic solvents, but can be attacked by strong oxidizing acids. At high temperature it becomes susceptible to attack by aromatic, chlorinated and aliphatic hydrocarbon. Due to the low amount of crystallinity, LDPE has a low melting point; it is at about 100 °C and the commercial LDPE has density in range of 0.915 – 0.930 g/cm^3. LDPE can be fabricated by many different methods for broad range of the applications, making it one of the most used plastics in world.

LLDPE is one of the PEs families which are having outstanding strength properties. LLDPE have been used in many application areas such as extruded film and coating, injection molding and rotational molding. It has a density between 0.915 and 0.925 g/cm^3. LLDPE with a wide range of short side chains generally has good impact, tensile and tear resistance, and its properties much depends on the type and the amounts of side chains branching. When comparing LLDPE with conventional LDPE with the same density and melt index properties, such as films or flexible molded products, they posses better impact, tear, toughness, chemically inert and resistant to solvents, acids and alkalies.

HDPE produced via low pressure process is found to be much stiffer than other type of polyethylene and having density in a range of about 0.940 – 0.970 g/cm^3. The increase in density and the stiffness is due to the much lower branching in HDPE backbone. HDPE has less then 15 (usually within the range of 1-6) short alkyl

branches per 1000 units of ethylene (Charles, 2010). This causes the HDPE macromolecule to have a high degree of crystallinity. Hence, HDPE considerably have improved mechanical properties, stiffer, harder and high strength compared to others PE grades. Besides, with high melting temperature (140 °C), it can be used to apply in high temperature condition and it only can be attacked by strong oxidizing agent at elevated temperature.

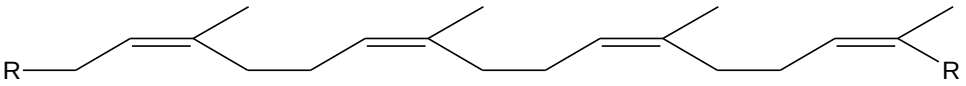
Typical uses of the various grades of polyethylene include:

- LDPE – packaging products, bags, films, garbage cans, industrial containers, piping and household items.
- LLDPE – wire and cable insulation, piping, bottles and films.
- HDPE – bottles, cans, house wares, toys, food containers, cases, pipes, bags, wire and cable coating and insulation for communication cable.

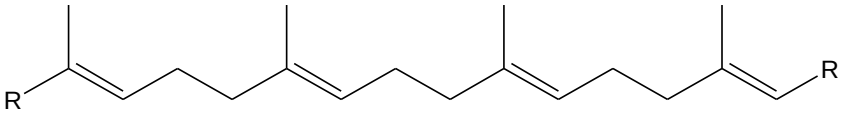
2.3.2 Occurrence and Structure of Natural Rubber

Natural rubber latex is collected as a colloidal suspension from *Havea brasiliensis* trees and later treated with formic acid to coagulate the rubber particle within the latex. The main constituent in natural rubber is poly (*cis*-1,4-isoprene), a highly unsaturated hydrocarbon. Natural rubber consists of isoprene unit (C_5H_8) in which each unit containing one double bond in the *cis* configuration (Figure 2.2). Although approximately 2000 of tree synthesize poly (*cis*-1,4-isoprene), only natural rubber from *Havea brasiliensis* (99% of world market) *and* gayule rubber of *Parthenium argentatum* (1% of world market) are produced commercially (Tanaka & Sakdapipanich, 2001). *Havea brasiliensis* has been established as most

commercially rubber source due to high yield annually and excellent properties of the rubber product.



Poly(*cis*-1,4-isoprene) = Natural rubber



Poly(*trans*-1,4-isoprene) = Gutta percha

Figure 2.2. Structural formula of polyisoprene.

Depending on the rubber clone, seasonal effects and the state of soil, an average natural rubber latex composition is as shown in Table 2.1 (Subramaniam, 1995). The rubber molecule present in latex is in the size of 3 μm – 5 μm, which is so called rubber particle and covered by a layer of proteins and lipids which separate the hydrophobic rubber from hydrophilic environment (Gomez and Moir, 1978). Upon acidification, usually with formic acid, rubber particles aggregate, assembling in percolating network or colloidal gel and later dehydrated to form solid NR. Dehydrated rubber contains 94 – 95% of hydrocarbon rubber, as well as about 2.8% acetone soluble fraction (fatty acid, sterols, tocotrienols, etc), 2.5% protein fraction and 0.2 % ash fraction mainly from magnesium and potassium phosphate (Bakhaus, 1985). In addition to the isoprene unit contained in *Havea brasiliensis*, others traces groups have also been reported such as esters (Eng et al., 1994), aldehydes (Subramaniam, 1977) and epoxides (Burfield, 1976). The increase of rubber viscosity during storage, also known as storage hardening is presumed to occur by crosslinking of these groups.

Table 2.1. Component's percentage in natural rubber latex (Subramaniam, 1995)

Latex Components	**Percentage (wt %)**
Polyisoprene	25 - 35
Protein	1 – 1.8
Carbohydrate	1 – 2
Neutral lipids	0.4 – 1.1
Polar lipids	0.5 – 0.6
Inorganic components	0.4 – 0.6
Amino acids, Amides, etc	0.4
Water	50 - 70

The most important factor governing the properties of NR is the stereoregularity of the polymer chains. The unique characteristic of NR is the ability to crystallize under strain, a phenomenon known as strain induced crystallization (Ver Strate & Lohse, 1994). Stretching of NR, which has almost *cis* configuration, leads to the crystallization and thus in turn leads to strengthening of the rubber. Another interesting property of NR is excellent tensile and tear properties and poses low hysteresis characteristics, which is an important requirement needed in heavy vehicle tyres. However, NR is not very resistant to oxidation, ozone weathering and wide range of chemicals and solvent, mostly due to unsaturated chains structure.

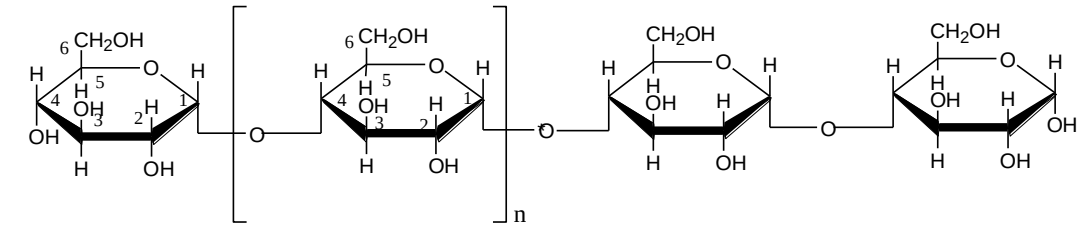
2.3.3 Structure and Nature of Starch

Starch is polysaccharide produced by mostly higher order plants as a storing energy. Commercially available starches nowadays are coming from the isolation of the grains such as corn, wheat and rice or from the tuber such as potato or tapioca. Chemically, starch is one type of the polysaccharide consisting of anhydroglucose unit and linked together through α-D-(1→4) glucosidic bond. Starch contains two main components, namely amylose which is linear and lightly branched comprising normally, 20 – 30% of the starch while the rest is amylopectin, a highly branched materials which is contributes to the crystalline segments of starch (Walstra, 2003). The approximate content of amylose from the different starch sources is presented in Table 2.2 (Datta, 2011).

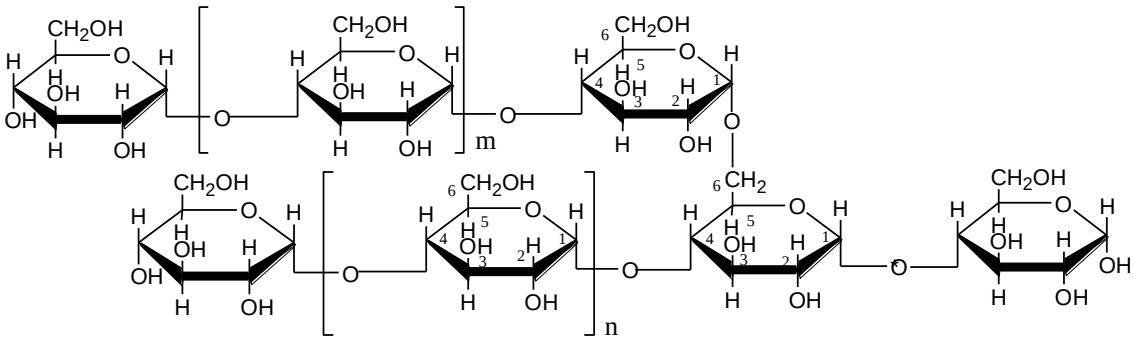
Table 2.2. Amylose content of various starches (Datta, 2011)

Starch Source	**Amylose (%)**
Cassava	17
Wheat	26
Sweat potato	18
Arrowroot	21
Sago	26
Potato	20
Corn	28
High amylose corn	70

Amylose is essentially built from the linear structure of α-1, 4 linked glucose unit whereas amylopection consist of short α-1, 4 chains linked by α-1, 4 bonds (Tester and Karkalas, 2002). Figure 2.3 shows the chemical structure of amylose and amylopectin.



(a)



(b)

Figure 2.3. Chemical structure of (a) amylose and (b) amylopectin (adapted fromTester and Karkalas, 2002).

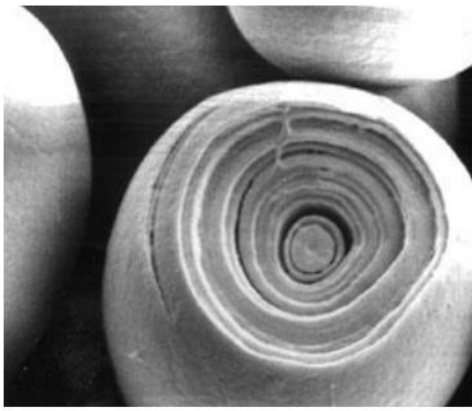
Amylose segments has a number average degree of polymerization (DP) of 1000 – 5000, whereas amylopectin with DP has around 10000 or more depending on the source of starch (Maningat et al., 2009). The linear segments of amylopectin are in the form of crystal while the amorphous region is formed by amylose and the residue of amylopectin at the branching points. Some important characteristics of amylose and amylopectin are summarized in Table 2.3 (Thomas and Atwell, 1997). Generally, most of the native starches are semi-crystalline with the crystallinity percentage at around 20 - 45% (Whistler et al., 1984). The degree of crystallinity of

starch not only depends on the type and the source of starch but also on the technique used and moisture content (Zobel, 1988; Buleon et al., 1982).

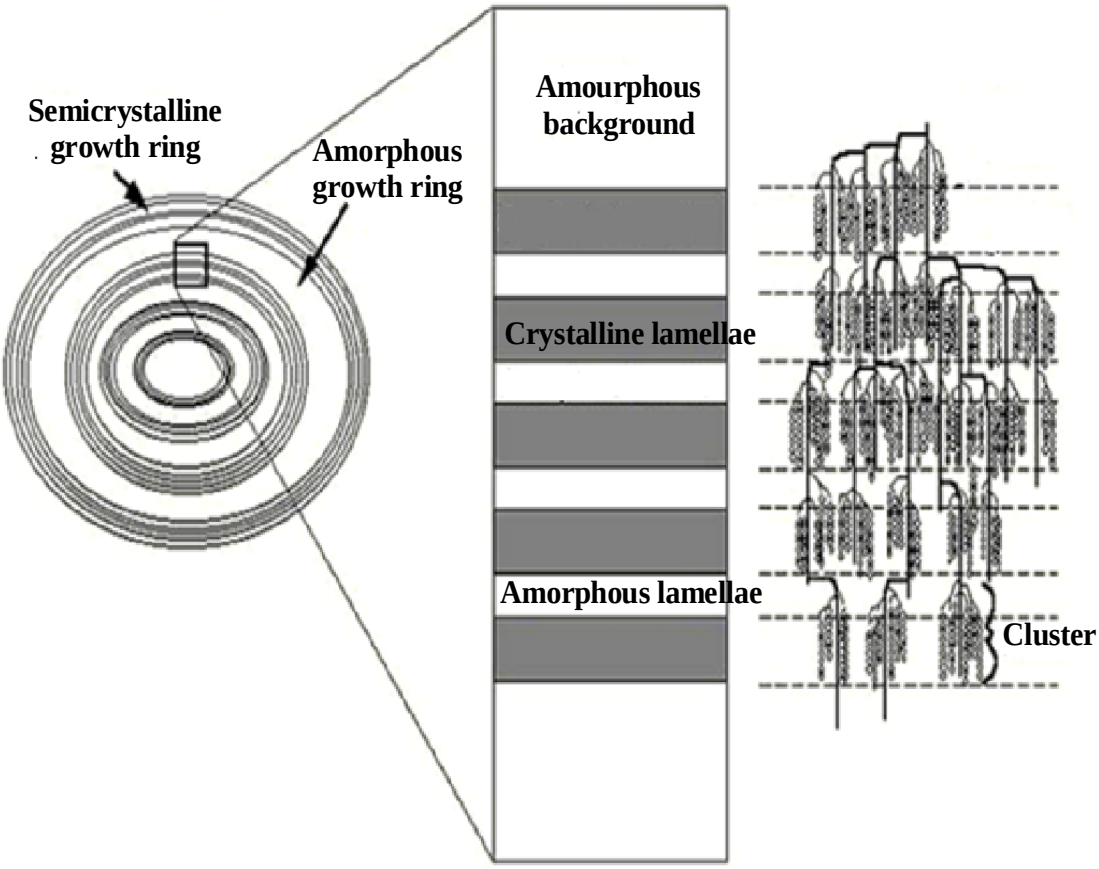
Table 2.3. Characteristics amylose and amylopectin (Thomas and Atwell, 1997).

Characteristic	**Amylose**	**Amylopectin**
Shape	Essentially linear	Branched
Linkage	α-(1→4); [some α-(1→6)-]	α-(1→4)and α-(1→6)
Molecular weight	Typically <0.5 million g/mol	50-500 million g/mol
Films	Strong	Weak
Gel formation	Film	Non gelling to soft
Colour with iodine	Blue	Reddish brown

From the photographic view, starch granules exhibit a so-called onion-like structure with the growth rings and can be readily visible under optical or electron microscopy (Figure 2.4 (a)). The size of starch granules is in the range of 5 µm - 100 µm where amylose and amylopectin are organized as alternating semi-crystalline and amorphous layer that form growth ring as shown in Figure 2.4 (b) (Jenkins and Donald, 1995). The semi-crystalline region consists of an ordered double helices formed by amylopectin short branches, while amorphous regions are composed from amylose and residue around the branches points of amylopectin (Biliaderis, 1992 and Godet et al., 1995). Similar to cellulose, melting behaviour of native starch is difficult to measure because it is above its decomposition temperature (Shogren, 1992).



(a)



(b)

Figure 2.4. (a) Photographic, and (b) Schematic view of the structure of a starch granule (Jenkins and Donald, 1995).